Heteroatom Directed Photoarylation. Synthetic Potential of the Heteroatom Sulfur

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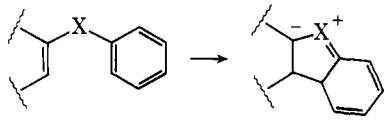
Abstract: Naphthyl vinyl sulfide **5** is prepared by acid-catalyzed addition–dehydration of 2-naphthalenethiol to ethyl acetoacetate. Photocyclization–rearrangement of **5** gives dihydrothiophene **6a**, which is desulfurized to **7a**; saponification of **7a** and polyphosphoric acid cyclodehydration of the resulting acid **7c** gives 2-ethyl-1-acenaphthone. A series of 2-thioaryloxyenones **11a–k** is prepared by reaction of the appropriate aromatic thiol with isophorone epoxide in the presence of base. Photocyclization–rearrangement of **11** gives dihydrothiophenes **12** in high yield; desulfurization of **12** with Raney nickel gives 3-arylcyclohexanones **13**, while reductive cleavage of **12** with zinc in acetic acid gives an ortho-substituted benzenethiol isolated in hemithioketal form **14**. Thioaryloxyenones **18**, **19**, **20a**, and **20b** are prepared from the appropriate thiol and the epoxide derived from 2-cyclopenten-1-one, $\Delta^{1(9)}$-octal-2-one, and $\Delta^{4(5)}$cholesten-3-one, respectively; these undergo photocyclization–rearrangement to give dihydrothiophenes. With fused ring thioaryloxyenones **19** and **20** only a *cis*-decalone ring fusion results; none of the corresponding trans isomer is detected. Acyclic thioaryloxyenones are not available via the epoxy ketone route; 3-thiophenoxy-4-methyl-3-penten-2-one (**26**) is prepared by reaction of 3-chloro-2,4-pentanedione with thiophenol in pyridine to give 3-thiophenoxy-2,4-pentanedione (**24**), followed by treatment with excess methylmagnesium bromide and finally acetic anhydride at reflux temperature. Irradiation of **26** gives dihydrothiophene **39** in 84% yield. A direct annelation route to **19** involves reaction of thiophenoxymethyl vinyl ketone (**44**) with the pyrrolidine enamine of cyclohexanone **45**. With modification of the annelation reagent, a variety of multicyclic ring systems with angular aromatic substituents should be available by the sequence cycloalkanone annelation–photocyclization–desulfurization. Dihydrothiophene **12a** undergoes regioselective alkylation of the equilibrium enolate to give **12b**, which is converted to sulfone **46c**. Reaction of **46c** with 1 N sodium hydroxide gives the ketone cleavage product carboxylic acid **48**, demonstrating that highly substituted aryl annelated dihydrothiophene 1,1-dioxides are available by methodology based on heteroatom directed photoarylation of aryl vinyl sulfides.

We wish to describe a new aromatic ring substitution process called *heteroatom directed photoarylation.* The methodological term heteroatom directed photoarylation is intended to characterize photochemically initiated, electrocyclic reactions originating from arrangements of an available electron pair in a heteroatom and the electrons from at least one aromatic π bond. The synthetic potential of the generalized photoreaction A → B, one example of heteroatom directed photoarylation, will be presented in this report. We will show that the photoreaction is quite general, proceeds with high chemical and photochemical efficiency, and is compatible with a wide variety of functional groups within the molecular system.



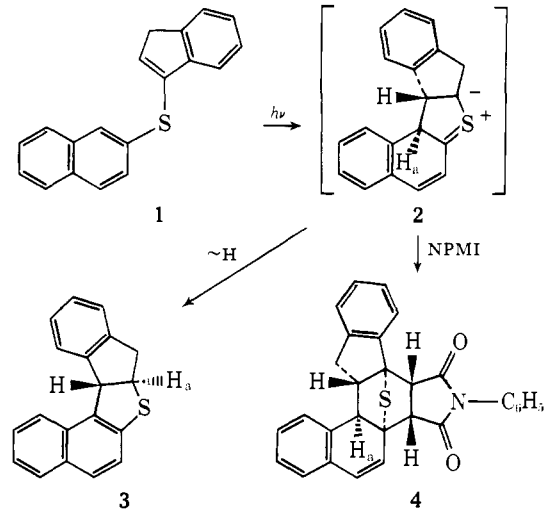
A B

Our studies began with an investigation of the photochemistry of 2-naphthyl vinyl sulfides.[3] Irradiation of a degassed benzene solution of 2-naphthyl-1-indenyl sulfide (**1**) gave *trans*-dihydrothiophene **3** in 78% isolated yield. Irradiation of **1** in the presence of the dipolarophile *N*-phenylmaleimide (NPMI, 2 equiv) resulted in isolation of a single cycloadduct **4** in 90% yield. Consideration of the stereochemistry in **3** and **4** demonstrates that cyclization of **1** is conrotatory to give the hypothetical thiocarbonyl ylide **2**,[3] and that hydrogen migration in **2** is suprafacial (and probably [1,4], involving H_a) to give the *trans*-dihydrothiophene **3**.

With an appreciation of the photocyclization mechanism, we turned our attention to development of the synthetic aspects of heteroatom directed photoarylation. The results of the study with the heteroatom sulfur are presented here.

Results and Discussion

An attractive feature of heteroatom directed photoarylation is the regiospecificity of aromatic substitution ortho to the heteroatom. Of particular note was the discovery that with aryl vinyl sulfides derived from 2-naphthalenethiol, only the dihydro[2,1-*b*]thiophenes are produced with no trace of the [2,3-*b*] isomers.[3] With prospects for regioselective control in mind, we investigated the use of the heteroatom as a temporary directing group for carbon–carbon bond formation, which could be removed in a subsequent step. The sulfur atom is ideally suited for this purpose because of the availability of a variety of desulfurization techniques. As one demonstration of this concept, 2-naphthalenethiol was converted to 2-ethyl-1-acenaphthone (**8**) (Scheme I).



1 2 3 4

Naphthyl vinyl sulfide **5** was prepared in 82% isolated yield, as an ~80:20 mixture of two double bond isomers, by the acid-catalyzed addition–dehydration of 2-naphthalenethiol to ethyl acetoacetate. Without separation of isomers, **5** was irradiated with Pyrex-filtered light in benzene solution. After >95% consumption of **5**, ^{1}H NMR analysis indicated ~30% dihydrothiophene **6a** and a substantial amount of polymeric material. On the other hand, **6a** could be isolated in 83% distilled yield (10-g scale) using Michler's ketone as a triplet

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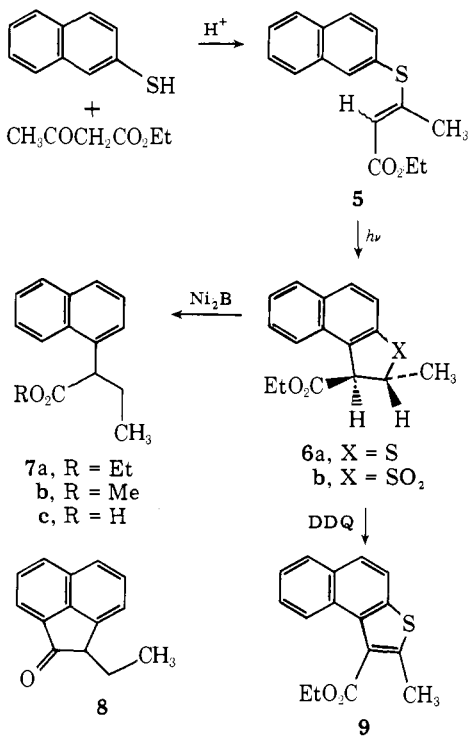
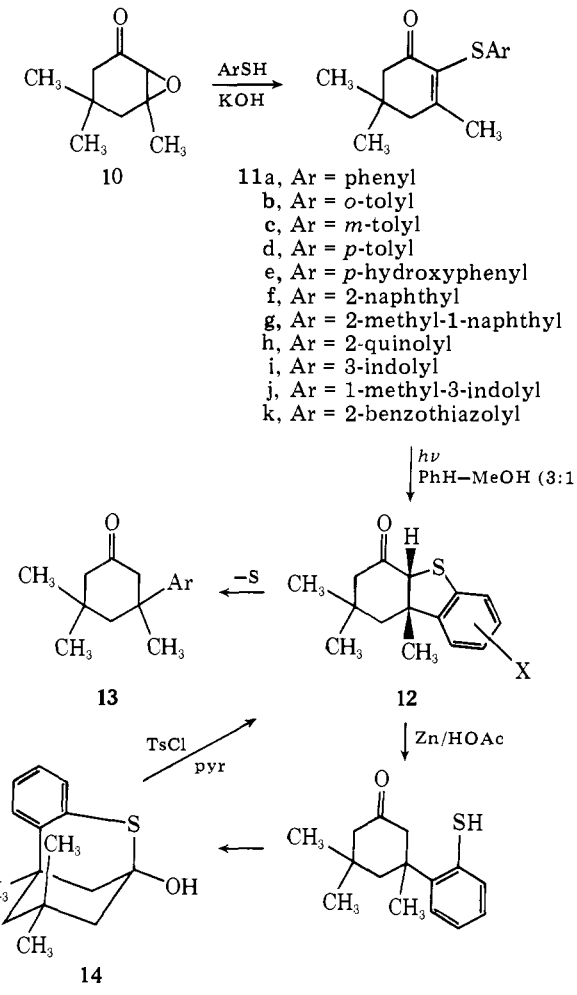
Scheme I



Scheme II



sensitizer. Dichlorodicyanoquinone (DDQ) dehydrogenation of **6a** gave the naphtho[2,1-*b*]thiophene **9**. The stereochemistry in **6a** was established by consideration of the dihydrothiophene ring vicinal proton coupling constants; J_{ab} = 2.5 Hz is consistent with trans dihydrostereochemistry in **6a**.[4] Peracid oxidation of **6a** gave the crystalline sulfone **6b** in high yield.

Desulfurization of **6a** with nickel boride[5] in refluxing ethanol gave **7a**. It is noteworthy that the conversion **5** → **7a** represents a new technique for the difficult task of introduction of an aryl nucleus α to an existing carbonyl group (CO_2Et).[6] Finally, saponification of **7a** and polyphosphoric acid cyclodehydration of the resulting carboxylic acid **7c** gave 2-ethyl-1-acenaphthone (**8**).

Introduction of an aryl substituent at a carbon atom β to a carbonyl group generally has been accomplished by conjugate addition of organocopper reagents to reactive α,β-unsaturated carbonyl compounds.[7] Unfortunately, competing 1,2-addition may occur and usually a two- or threefold excess of organocopper reagent is required for satisfactory conjugate addition. We have devised an efficient and experimentally simple alternative as shown in Scheme II.[8]

The epoxidation of an α,β-unsaturated ketone may be performed with basic hydrogen peroxide, and the resulting epoxy ketone serves as a convenient precursor to cyclic 2-thioaryloxyenones (e.g., **10** → **11**). Thus, reaction of aryl mercaptans with epoxide **10**[9] in ethanol and a catalytic amount of potassium hydroxide under a nitrogen atmosphere gave 2-thioaryloxyenones **11** in isolated yields generally >90%. The reaction proceeds under extremely mild conditions to give **11** free of the isomeric **17**. Formation of **17** might have occurred as shown below via diketone enolate **16**; in principle, cyclization-dehydration of **16** could give either **11** or **17**. We note that whereas **11** has a tetrasubstituted carbon-carbon double bond, that in **17** is only trisubstituted.[10] Apparently, when the substituent at the β carbon atom in the epoxy ketone is no larger than methyl, the conversion to 2-thioaryloxyenone occurs in high yield. We will demonstrate that in certain cases an alkyl group larger than methyl leads to isomeric mixtures of analogues of **11** and **17**.[11]

The epoxy ketone to 2-thioaryloxyenone conversion also is useful with cyclopentenone epoxides; reaction of 1-naphthalenethiol with cyclopentenone epoxide gave **18** in 90% isolated yield. The exclusive formation of **18** demonstrates the high degree of regioselectivity in the position of epoxide opening. Clearly the reaction is not directed by steric consid-

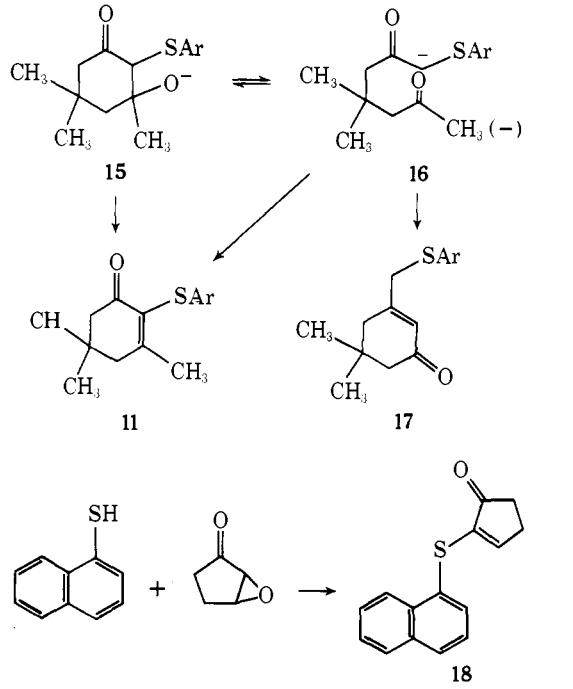


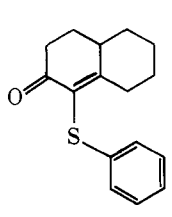
Table I. Photocyclization of Thioaryloxyenones to Dihydrothiophenes

Thioaryloxyenone	Dihydrothiophene	% yield[a]
11a	**12a**	91
11b	**12b**	88
11c	**12c**	92[b]
11d	**12d**	84
11e	**12e**	83
11f	**12f**	89
11g	*c*	
11h	**12h**	78
11i	*c*	
11j	**12j**	63
11k	*c*	
18	**33**	86
19	**35**	95
20a	**38a**	90
20b	**38b**	69
26	**39**	84

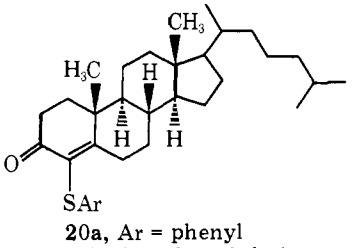
[a] Represents isolated yield of distilled or crystallized product. [b] Ratio of isomers is 70:30. [c] A dihydrothiophene was not observed.

erations, because in the case of cyclopentenone epoxide there is equal substitution at both epoxide carbon atoms.[12]

Epoxy ketones derived from $\Delta^{1(9)}$-octal-2-ones also may be converted to thioaryloxyenones (e.g., **19** and **20**) in high yield.

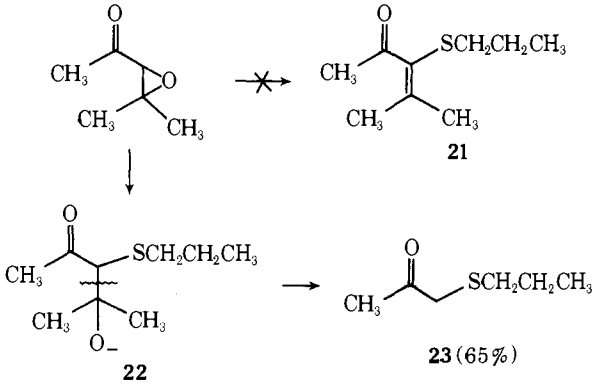


19



20a, Ar = phenyl
b, Ar = 2-naphthyl

However, the reaction is not applicable to acyclic epoxy ketones. Attempted preparation of **21** from mesityl oxide epoxide and *n*-propyl mercaptan gave instead keto sulfide **23**, presumably via cleavage of intermediate **22**.

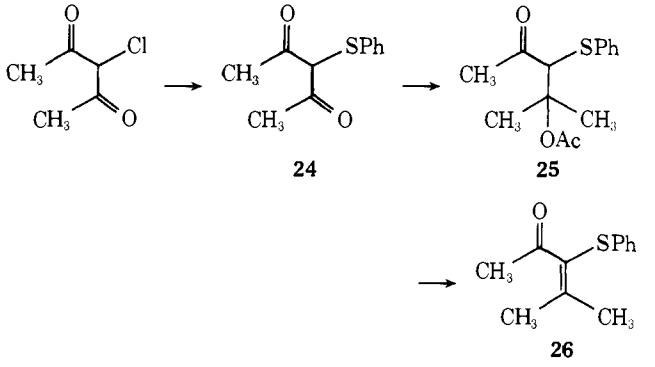


22

23 (65%)

Acyclic thioaryloxyenones may be prepared in high yield from α-halo-β-dicarbonyl compounds by a modification of a procedure described by Büchi and Wüest.[13] For example, the synthesis of **26** begins by reaction of 3-chloro-2,4-pentanedione with thiophenol in pyridine to give 3-thiophenoxy-2,4-pentanedione (**24**). Treatment of **24** with 1 equiv of sodium hydride in ether followed by addition of methylmagnesium bromide and finally excess acetic anhydride gave the β-acetoxy ketone **25** (not isolated). Heating the reaction mixture for 2.5 h and workup gave **26** in 75% isolated yield from **24**.

Pyrex-filtered irradiation of 2-thioaryloxyenones **11** in benzene–methanol solution (3:1) in a conventional preparative

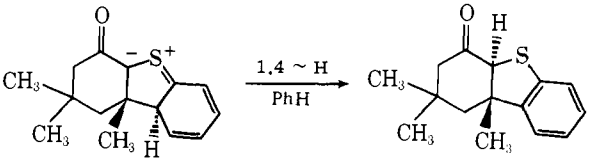


24 **25** **26**

photoreactor generally gave the cis-fused dihydrothiophenes **12** in excellent yield (Table I). The photochemical efficiency of the cyclization must be exceptionally high; consequently, *the process is applicable to large-scale synthesis and reactant concentrations ≥0.1 M may be conveniently employed.* For example, 70 g of **11a** in 2000 mL of solution was converted into 64 g of **12a** in <20 h irradiation with a 450-W mercury arc lamp.

Irradiation of **11a** in degassed benzene solution (0.05 M) for 2 h gave, in addition to **12a** (27%, ^{1}H NMR analysis), *trans*-dihydrothiophene **27b** (27%) and thioaryloxyenone **11a** (6%). The ^{1}H NMR spectrum of **27b** is characterized by sharp singlets at δ 1.22 (6 H), 1.26 (3 H), and 4.71 (1 H). The photoreaction mixture was treated with sodium carbonate in benzene–methanol (1:1) solution at room temperature, after which solvent evaporation and ^{1}H NMR analysis of the crude reaction mixture indicated the complete disappearance of **27b** along with formation of additional **12a** (53%).

From these data, we conclude that in benzene solution, **11a** experiences conrotatory photocyclization to thiocarbonyl ylide **27a**, from which suprafacial 1,4-hydrogen migration gives the



27a **27b**

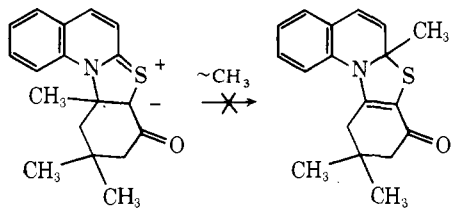
strained trans-fused dihydrothiophene **27b**. Hydrogen migration in **27a** may be stereospecific to give only **27b**, from which the more stable **12a** is generated by epimerization. In related studies with aryloxyenones, we have demonstrated that photocyclization–rearrangement is, in fact, stereospecific to give only *trans*-dihydrofurans.[11,17]

Assignment of stereochemistry in dihydrothiophenes is based on the observed epimerization of **27b** to **12a** (vide supra); the cis isomer represents the stable configuration of a fused five- or six-membered ring system capable of epimerization.[14] Stereochemistry of all other photoproducts considered here follows from ^{1}H NMR spectral data; a characteristic resonance for the C(2) methine proton in *cis*-dihydrothiophenes appears at ~δ 3.8, while that in *trans*-dihydrothiophene **27b** gives a resonance at δ 4.71.

It should be noted that product yields for photocyclization of **11a** in protic solvents were significantly higher than those in pure benzene. Consequently, all subsequent photoreactions of thioaryloxyenones were performed in benzene–methanol (3:1), and *cis*-dihydrothiophenes were the isolated photoproducts.

With ortho- and para-substituted thiophenoxyenones **11b, 11d,** and **11e** the photoreaction is completely regioselective; with the meta-substituted **11c,** however, cyclization gives a 70:30 mixture of isomers. In this case, carbon–carbon bond formation ortho to the methyl substituent predominates.

The exclusive formation of **12f** from **11f** once again[3] demonstrates that with 2-naphthyl vinyl sulfides, cyclization occurs only at C(1) and not C(3). The 2-quinolyl derivative **11h** is interesting, because cyclization at the 1 position in the quinoline ring requires carbon–nitrogen bond formation and would give intermediate ylide **28a**. Subsequent rearrangement **28a** → **28b** via a 1,4 methyl migration to C(2) would result in a net

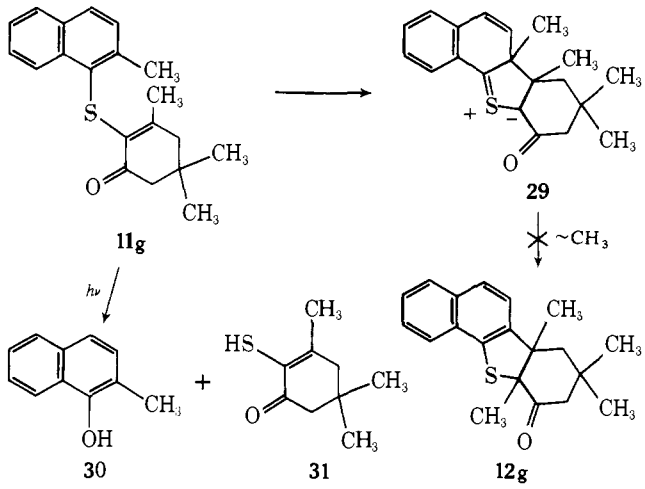


28a **28b**

loss of aromaticity. Instead, cyclization occurs at C(3) and dihydrothiophene **12h** is isolated in 78% yield.

N-Methylindoles also undergo heteroatom directed photoarylation as demonstrated by the conversion **11j** → **12j**. However, irradiation of N-substituted **11i** gave mainly polymerization in both protic and aprotic (benzene) solvents.

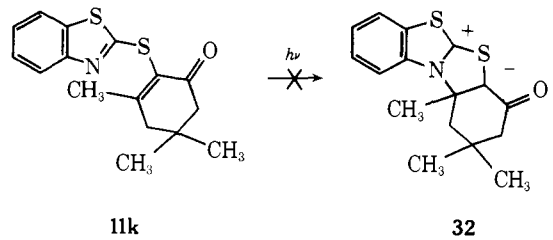
The 2-methyl-1-naphthyl vinyl sulfide **11g** was prepared in order to determine if dihydrothiophene **12g** would be produced by cyclization to thiocarbonyl ylide **29** followed by a 1,4-methyl migration. Although we can say little about the cyclization **11g**



11g **29** **30** **31** **12g**

→ **29**, no **12g** was detected in photoreactions of **11g**. In benzene solution, **11g** undergoes slow polymerization and in benzene–methanol **11g** experiences photohydrolysis to give 2-methyl-1-naphthol (**30**) and keto enethiol **31** in high yield. The preparation of enethiols by photohydrolysis of aryl vinyl sulfides may be synthetically useful and we are currently investigating this possibility.

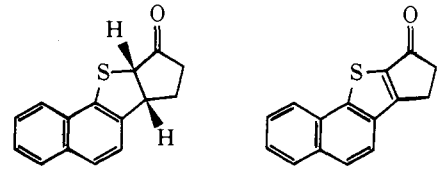
We attempted to generate a stable thiocarbonyl ylide (e.g., **32**) from the 2-mercaptobenzothiazole derived vinyl sulfide **11k**. Hypothetical ylide **32** presumably would be stabilized by



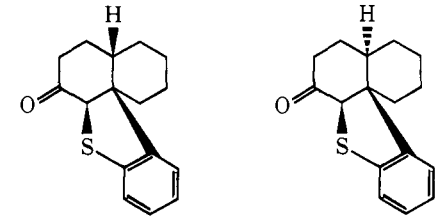
11k **32**

both electron-donating and -withdrawing groups. This kind of electronic stabilization of zwitterionic molecules is well documented.[15] With **11k**, however, Pyrex-filtered irradiation did not lead to detection of **32** (UV-visible and ^{1}H NMR spectroscopy), but rather only to slow photopolymerization. Thus, photoinitiated carbon–nitrogen bond formation (unless rapidly reversible) does not occur with **11k** or the 2-quinolyl derivative **11h**.

Pyrex-filtered irradiation of aryl vinyl sulfide **18** in benzene–methanol solution (1:1) gave dihydrothiophene **33** in 86% crystallized yield.[16] Thus, a ring C heterosteroid analogue is available in two simple steps from 1-naphthalenethiol in 78% overall yield. The photocyclization **18** → **33** also demonstrates that (1) 1-naphthyl vinyl sulfides undergo heteroatom directed photoarylation exclusively at C(2); (2) a cyclopentenone will participate in the photocyclization; and (3) cyclic 2-thioaryloxyenones need not be substituted at C(3) for effective isolation of dihydrothiophenes. We do note, however, that oxygen must be rigorously excluded from the photolysis solution and irradiation must be discontinued after ~98% consumption of **18**, or substantial amounts of dehydrogenation of **33** to thiophene **34** will result.

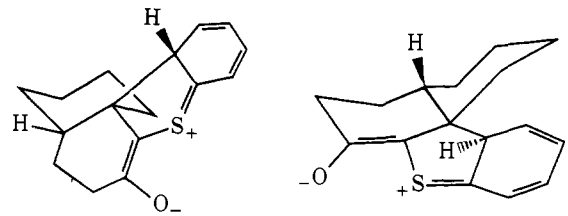


33 **34**



35 **36**

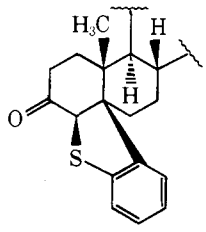
The stereochemical control possible with heteroatom directed photoarylation is exceptionally high as demonstrated by conversion of 2-thiophenoxyoctalone **19** to dihydrothiophene **35** in >95% yield. The decalone ring system in **35** was shown to have a cis fusion (vide infra), and none of the dihydrothiophene **36** with a *trans*-decalone ring system could be detected. Initially, we hypothesized that stereochemistry resulting from cyclization of a vinyl sulfide in a fused ring system might be controlled by steric influences.[8] Our subsequent detailed studies[11,17] of related photocyclizations involving the heteroatom oxygen suggest that ring strain arguments may provide a better explanation here. Thus, the remarkable stereoselectivity in the photocyclization **19** → **35** could be a result of relative ring strain in thiocarbonyl ylides **37a** and **37b**, which



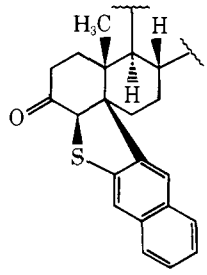
37a **37b**

are hypothetical intermediates resulting from the two possible conrotatory cyclization modes available to photoexcited **19**. It is clear that a planar π-electron system in **37** imposes a great deal of ring strain in configuration **37b**, which would lead to the trans-fused decalone **36**, but relatively little in **37a**. On the basis of unfavorable ring strain in intermediates such as **37b**, we suggest that photocyclization of 1-thioaryloxy-$\Delta^{1(9)}$-octal-2-ones should produce dihydrothiophenes with *cis*-decalone ring fusions. In support of this generalization,[11] we note

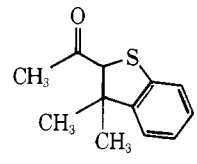
that steroid derivatives **20a** and **20b** undergo cyclization to the cis-fused decalones **38a** and **38b** in high yield.



38a



38b



39

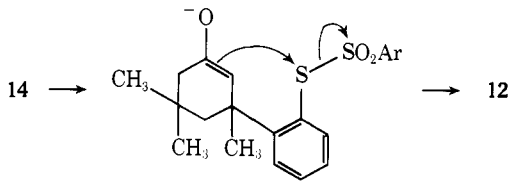
Photocyclization studies with acyclic thioaryloxyenone **26** reveal some interesting solvent effects on the photochemical efficiency of product formation. Irradiation of **26** in benzene–methanol solution (1:1) gave dihydrothiophene **39** in >90% yield. In benzene solution under similar conditions, **26** was recovered with <5% **39** formed. With polar aprotic solvents such as methylene chloride, chloroform, or acetonitrile 40–50% **39** was produced.[16] This solvent dependence, which was not observed in the photochemistry of cyclic thioaryloxyenones, may provide information concerning the character of the reactive excited state in **26**[18] and is currently under study.

Returning to the methodological concept expressed in Scheme II, the conversion of dihydrothiophenes **12** to ketone β-arylation products **13** was best accomplished by desulfurization with Raney nickel in refluxing ethanol solution. While partial to complete hydrogenation of the carbonyl group in **12** accompanied desulfurization, treatment of the crude desulfurization product with Jones reagent generally gave ketones **13** in ~85% overall yields.

No reduction of the aromatic ring occurred with benzoannelated dihydrothiophenes **12a–e**; however, desulfurization of **12f** with Raney nickel or nickel boride[5] resulted in extensive reduction of the naphthalene ring. Refluxing the desulfurized ketone with excess DDQ in benzene solution gave 3-(α-naphthyl)-3,5,5-trimethylcyclohexanone **13f** in 50% overall yield.

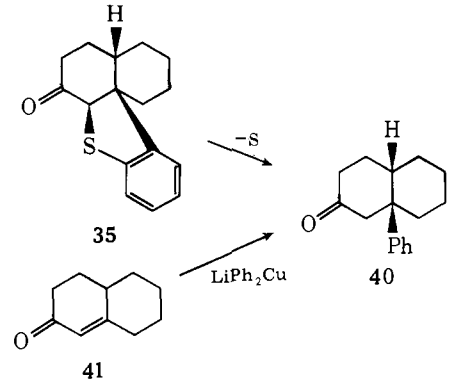
Dihydrothiophenes **12** suffer metal-promoted, reductive cleavage of the C(2)–sulfur bond. For example, **12a** was converted to an ortho-substituted thiophenol, isolated in hemithioketal form **14,** on treatment with zinc dust in refluxing acetic acid solution (94% isolated yield). The three-step sequence thiophenol → **11a** → **12a** → **14** occurs in 82% overall isolated yield and represents an important new method for enone β-(*o*-mercaptophenylation).

We have made the interesting observation that treatment of **14** with *p*-toluenesulfonyl chloride in refluxing pyridine solution regenerates dihydrothiophene **12** in essentially



quantitative yield. This oxidative cyclization presumably involves intramolecular enolate displacement of $ArSO_2^-$ from an intermediate thiotosylate as shown.

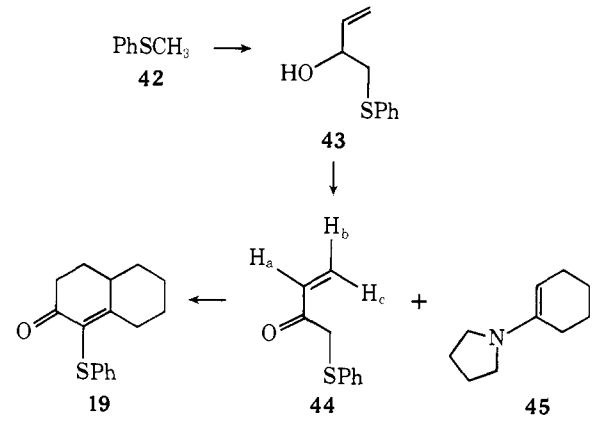
Desulfurization of dihydrothiophene **35** gave only *cis*-9-phenyldecalone-2 in high yield, which was identified by direct comparison with the product previously characterized from addition of lithium diphenylcuprate to $\Delta^{1(9)}$-octalone-2 (**41**).[19] By inference, the conversion **35** → **40** demonstrates that stereochemistry of the decalone ring fusion in **35** is cisoid (vide supra).



35 **40** **41**

We have devised a direct annelation route to **40,** which should be generally useful in construction of complex multicyclic ring systems with an aryl substituent at a ring junction carbon atom (Scheme III). Thus, thiophenoxymethyl vinyl

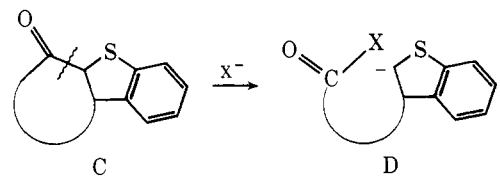
Scheme III



42 **43** **19** **44** **45**

ketone **44** was prepared from thioanisole **42**[20] as shown. Annelation of the pyrrolidine enamine of cyclohexanone **45**[21] gave thioaryloxyenone **19,** previously prepared by the epoxy ketone route (vide supra). With appropriate modification of the annelation reagent,[22] a variety of multicyclic ring systems with angular aromatic substituents should be available by the methodology presented in Schemes II and III.

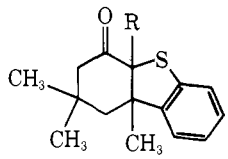
In order to extend the synthetic utility of heteroatom directed photoarylation, we considered the possibility of effecting nucleophilic cleavage of the cycloalkanone C(1)–C(2) bond (e.g., C → D). Attempts at hydroxide cleavage of the acyl bond



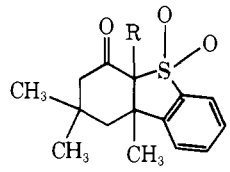
C D

in dihydrothiophene **12a** (X = OH) were ineffective, suggesting that the more reactive keto sulfone **46a** would be required.

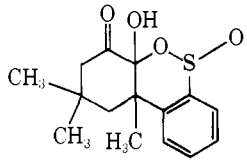
Reaction of **12a** with *m*-chloroperbenzoic acid did not give **46a,** but rather resulted in a complex mixture of products. On the other hand, treatment of **12a** with Jones reagent gave a single product in 88% isolated yield. The electron impact mass spectrum (*m/e* 294) and IR data (2.83, 5.82, 7.75, and 9.00 μ; Nujol) indicated that hydroxy keto sulfone **46b** had formed. Furthermore, examination of the ^1H NMR spectrum for **46b** showed that the C(2) methine proton had been replaced by a broadened singlet (1 H) at δ 5.2 and that this resonance disappeared on exchange with deuterium oxide.



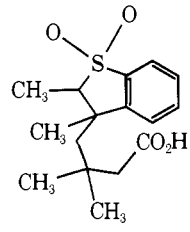
12a, R = H
b, R = CH_3



46a, R = H
b, R = OH
c, R = CH_3



47



48

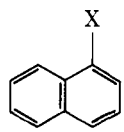
Refluxing **46b** in 1 N sodium hydroxide solution followed by acidification to pH <2 with 1 N hydrochloric acid gave cyclic sulfinate ester **47** (IR 8.99 μ)[23] in high yield.

Enolate stabilization by sulfur is well documented; consequently, we felt that alkylation of the equilibrium enolate mixture derived from **12a** should occur predominantly at C(2). Reaction of a slight excess of **12a** with potassium hydride[24] in THF solution followed by addition of methyl iodide gave **12b** in 72% crystallized yield, and oxidation of **12b** with Jones reagent gave sulfone **46c**.

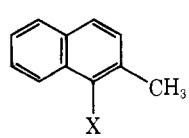
In contrast to **12a** or **46b,** keto sulfone **12b** reacted with 1 N sodium hydroxide to give, after acidification, carboxylic acid **48** in excellent yield. Thus, the alkylation–oxidation–cleavage sequence demonstrated with **12a** should be applicable to synthesis of a variety of highly substituted aryl annelated dihydrothiophene 1,1-dioxides.

The application of heteroatom directed photoarylation to aryl vinyl sulfides is dependent on the availability of aromatic thiols. Fortunately, many simple, high-yield methods have been described and we note three of these used for preparation of thiols required by this study.

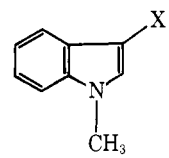
Naphthalene undergoes kinetic sulfonation with concentrated sulfuric acid at C(1) to give 1-naphthalenesulfonic acid (**49a**) in approximately quantitative yield. The reaction is reversible and at higher temperatures 2-naphthalenesulfonic acid predominates. Conversion of **49a** to sulfonyl chloride **49c** via reaction of sodium salt **49b** with phosphorus pentachloride and finally reduction of **49c** with zinc in acetic acid gives 1-naphthalenethiol in high overall yield.[25]



49a, X = SO_3H
b, X = SO_3Na
c, X = SO_2Cl
d, X = SH



50a, X = Br
b, X = SH



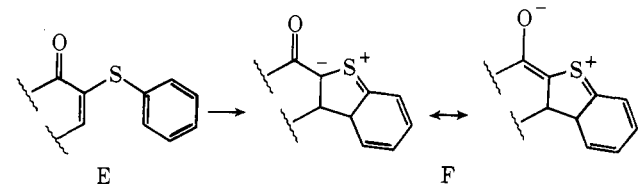
51a, X = H
b, X = SH

Aryl Grignard reagents react with sulfur to give magnesium salts of aryl mercaptans.[26] Thus, 1-bromo-2-methylnaphthalene (**50a**) affords 2-methyl-1-naphthalenethiol in 61% distilled yield (see Experimental Section). We have prepared a variety of substituted aromatic thiols using Grignard and aryllithium[27] reagents and yields have been good to excellent.

Thiol **51b,** used in synthesis of vinyl sulfide **11j,** was conveniently prepared from 1-methylindole **51a**.[28] Reaction of **51a** with thiourea and iodine–potassium iodide gives a thiouronium salt, from which thiol **51b** can be isolated by sequential treatment with strong base and mineral acid.

Conclusion

Heteroatom directed photoarylation is a useful method for construction of a variety of aryl annelated dihydrothiophenes. With 2-thioaryloxyenones, photocyclization (e.g., E → F)



E F

occurs with Pyrex-filtered light generally in excellent chemical yield and with high photochemical efficiency. We feel that the remarkable facility with which thiocarbonyl ylides are formed may be a result of stabilization of the intermediate as shown in F.

The dihydrothiophenes prepared by heteroatom directed photoarylation undergo a variety of high-yield, synthetically useful transformations. In this regard, methods for carbonyl α- and β-arylation have been developed.

Benzoannelated dihydrofurans are common to many medicinally important natural products, and the high degree of success with the heteroatom sulfur prompted an investigation of the photochemistry of aryl vinyl ethers. The results of the study with the heteroatom oxygen are presented in the accompanying paper.

Experimental Section

General. Photoreactions were performed in sealed Pyrex tubes containing 3.2 mL of solution degassed by four freeze–pump–thaw cycles with an oil-diffusion-pump vacuum (vacuum monitored by means of a calibrated Varian NRC-802A thermocouple vacuum gauge). A Hanovia 450-W medium-pressure mercury arc lamp placed in a water-cooled Pyrex well was used as the light source. Preparative-scale photoreactions were performed in a conventional 350-mL capacity photoreactor under an argon atmosphere. Irradiation solvents were in general spectral grade and were used without further purification.

^1H NMR spectra were obtained on a Varian A-60A NMR spectrometer (tetramethylsilane internal standard; deuteriochloroform solvent). Low-resolution chemical ionization and electron impact mass spectra were obtained with a Finnigan 3300 gas chromatograph–mass spectrometer, while high-resolution mass measurements were made with an AEI-MS-9102 mass spectrometer. Infrared spectra were recorded on a Perkin-Elmer Model 137B infrared spectrometer and a calibrated Thomas-Hoover capillary melting point apparatus was used for melting point determinations. An F & M Model 700 gas chromatograph was used for VPC analysis. Microanalyses were carried out by Spang Microanalytical Laboratory, Ann Arbor, Mich.

2-(2-Naphthylthio)-1-carboethoxy-1-propene (5). A solution of 2-naphthalenethiol (10.0 g, 62.5 mmol), ethyl acetoacetate (9.0 mL, 69.2 mmol), and *p*-toluenesulfonic acid (100 mg) in benzene (100 mL) was refluxed in a dry nitrogen atmosphere until the calculated amount of water was collected in a water separator. Evaporation of solvent and distillation gave **5** (13.8 g, 82%, bp 145–158 °C at 0.1 mm) as a mixture (~80:20) of two double bond isomers: ^1H NMR for the major isomer δ 1.15 (3 H, triplet, J = 7.0 Hz), 2.48 (3 H, doublet, J = 1.0 Hz), 4.07 (2 H, quartet, J = 7.0 Hz), 4.07 (2 H, quartet, J = 7.0 Hz), 5.35 (1 H, quartet, J = 1.0 Hz), and 7.2–8.1 (7 H, multiplet), and for the minor isomer δ 1.30 (3 H, triplet, J = 7.0 Hz), 1.83 (3 H, doublet, J = 1.0 Hz), 4.26 (quartet, J = 7.0 Hz), 5.90 (1 H, quartet, J = 1.0 Hz), and 7.2–8.1 (7 H, multiplet); electron impact mass spectrum of isomeric mixture *m/e* 272.

Irradiation of 2-(2-Naphthylthio)-1-carboethoxy-1-propene (5). A solution of **5** (10.0 g) and Michler's ketone (100 mg) in benzene (350

mL) was purged with argon for 20 min and irradiated with Pyrex-filtered light, while a slow stream of argon was passed into the solution. After ~100 h of irradiation, solvent was evaporated and the crude reaction product was distilled to give **6a** (8.30 g, 83%, bp 169 °C at 0.1 mm) contaminated with a small amount of **5** (3–5%): ^{1}H NMR δ 1.13 (3 H, triplet, J = 7.0 Hz), 1.52 (3 H, doublet, J = 7.0 Hz), 4.15 (2 H, quartet, J = 7.0 Hz) superimposed on an undefined multiplet (1 H), 4.42 (1 H, doublet, J = 2.5 Hz), and 7.1–8.0 (6 H, multiplet); IR (neat) 5.79 μ (s).

Peracid Oxidation of 6a. A solution of **6a** (350 mg, 1.3 mmol) and *m*-chloroperbenzoic acid (0.58 g, 85% active, ~2.2 equiv) in methylene chloride (10 mL)–ether (10 mL) was stirred at room temperature for 6 h. Methylene chloride (50 mL) was added and the resulting solution was washed with 1 N sodium carbonate (4 × 20 mL), dried over anhydrous magnesium sulfate, and evaporated. Crystallization from ether–petroleum ether gave **6b** (317 mg, 81%, mp 108–110 °C): ^{1}H NMR δ 1.19 (3 H, triplet, J = 7.0 Hz), 1.62 (3 H, doublet, J = 7.0 Hz), 3.90 (1 H, partially resolved eight-line multiplet, J = 7 and J' = 5.0 Hz), 4.27 (2 H, partially resolved quartet, J = 7.0 Hz), 4.40 (1 H, partially resolved doublet, J = 5.0 Hz), and 7.5–8.2 (6 H, multiplet); IR (Nujol) 5.78 (s), 7.67 (s), and 8.92 μ (s); electron impact mass spectrum *m/e* 304.

Anal. Calcd for $C_{16}H_{16}SO_4$: C, 63.15; H, 5.30. Found: C, 63.05; H, 5.24.

Dichlorodicyanoquinone (DDQ) Dehydrogenation of 6a. A solution of **6a** (1.0 g, 3.68 mmol) and DDQ (0.95 g, 4.28 mmol) in benzene (10 mL) was refluxed in a nitrogen atmosphere for 5 h. Benzene (25 mL) was added and the resulting solution was washed with 1 N sodium carbonate (3 × 20 mL), dried over anhydrous magnesium sulfate, and evaporated. Distillation (bp 160–162 °C at 0.1 mm, 0.75 g, 76%) and crystallization from ethanol gave **9** (mp 65–67 °C): ^{1}H NMR δ 1.40 (3 H, triplet, J = 7.0 Hz), 2.61 (3 H, singlet), 4.55 (2 H, quartet, J = 7.0 Hz), and 7.2–8.4 (6 H, multiplet); IR (neat) 5.81 μ (s); electron impact mass spectrum *m/e* 270.

Desulfurization of 6a. Nickel boride was prepared by the method of Truce and Perry[5] and desulfurization of **6a** in refluxing ethanol solution (20 h) gave after distillation **7a** (bp 116–118 °C at 0.07 mm, 91%): ^{1}H NMR δ 0.94 (3 H, partially resolved triplet, J = 7 Hz), 1.06 (3 H, partially resolved triplet, J = 7 Hz), 2.1 (2 H, quintet, J = 7.0 Hz) 4.08 (2 H, partially resolved quartet, J = 7 Hz), 4.28 (1 H, partially resolved triplet, J = 7.0 Hz), and 7.0–8.3 (7 H, multiplet); IR (neat) 5.79 μ (s). Because of the complex NMR spectrum, **6a** was converted to methyl ester **6b**. A solution of **6a** (150 mg) in methanol (40 mL) with concentrated sulfuric acid (3 drops) was heated to reflux (20 h). Evaporation of solvent, addition of ether (50 mL), washing with 1 N sodium carbonate solution (1 × 10 mL), drying over anhydrous magnesium sulfate, and evaporation of solvent gave essentially pure **6b** as judged by the ^{1}H NMR spectrum: δ 0.93 (3 H, triplet, J = 7.0 Hz), 2.1 (quintet, 2 H, J = 7 Hz), 3.58 (3 H, singlet), 4.29 (1 H, triplet, J = 7.0 Hz), and 7.0–8.3 (7 H, multiplet); electron impact mass spectrum (**6a**) *m/e* 242.

Conversion of 7a to 1-Acenaphthone 8. A solution of **7a** (150 mg) in methanol (5 mL)–1 N sodium hydroxide (5 mL) was refluxed for 5 h. Acidification with 1 N hydrochloric acid, ether extraction (3 × 25 mL), drying over anhydrous magnesium sulfate, and evaporation of solvent gave **7c**: IR (neat) 2.8–4.3 (s) and 5.86 μ (s). To the crude carboxylic acid **7c** was added polyphosphoric acid (10 mL) and the resulting mixture was stirred and heated to 90 °C for 10 h. Addition of water, extraction with ether, and evaporation of solvent gave an oil. Thick layer chromatography (silica gel, benzene solvent) gave pure **8** (oil, 80 mg, 66%): ^{1}H NMR δ 0.92 (3 H, triplet, J = 7.0 Hz), 2.1 (2 H, broadened quintet), 3.69 (1 H, triplet, J = 6 Hz), and 7.2–8.2 (6 H, multiplet); IR (neat) 5.84 μ (s).

2-Phenylthio-3,5,5-trimethyl-2-cyclohexen-1-one (11a). General Procedure for 2-Thioaryloxyenone Formation from Epoxy Ketones. A solution of isophorone epoxide (**10**,[9] 50.0 g, 0.324 mol) in ethanol (100 mL) and 15% potassium hydroxide (5 mL) solution was stirred at ice-bath temperature in a nitrogen atmosphere,[29] while a solution of benzenethiol (35.6 g, 0.324 mol) in freshly distilled THF (100 mL) was added over ~30 min. After stirring at 0 °C for ~8 h, water (200 mL) was added to the light orange solution. Extraction with ether–benzene (1:1, 3 × 200 mL), washing the organic layer with saturated sodium chloride solution (2 × 50 mL), drying over anhydrous magnesium sulfate, solvent removal, and crystallization from ether–petroleum ether gave 2-phenylthio-3,3,5-trimethyl-2-cyclohexen-1-one (71.8 g, 90%, mp 55–56 °C): ^{1}H NMR gave singlets at δ 1.08 (6 H), 2.26 (3 H), 2.41 (2 H), 2.48 (2 H), and 7.18 (5 H); IR (Nujol) 5.99 (s), 6.18 (m), and 6.31 μ (s); electron impact mass spectrum *m/e* 246.

2-(*o*-Tolylthio)-3,5,5-trimethyl-2-cyclohexen-1-one (11b) was prepared from *o*-tolylthiol and epoxide **10** (96%, bp 148–150 °C at 0.05 mm); ^{1}H NMR gave singlets at δ 1.08 (6 H), 2.23 (3 H), 2.40 (2 H), 2.44 (3 H), 2.49 (2 H), and a multiplet at 6.7–7.2 (4 H).

2-(*m*-Tolylthio)-3,5,5-trimethyl-2-cyclohexen-1-one (11c) was prepared from *m*-tolylthiol and epoxide **10** and crystallized from ether–petroleum ether (92%, mp 80–83 °C); ^{1}H NMR gave singlets at δ 1.08 (6 H), 2.27 (6 H), 2.41 (2 H), 2.49 (2 H), and a multiplet at 6.8–7.2 (4 H).

2-(*p*-Tolylthio)-3,5,5-trimethyl-2-cyclohexen-1-one (11d) was prepared from *p*-tolylthiol and epoxide **10** (98%, bp 148–149 °C); ^{1}H NMR gave singlets at δ 1.08 (6 H), 2.29 (6 H), 2.41 (2 H), 2.48 (2 H), and 7.10 (4 H).

2-(*p*-Hydroxyphenylthio)-3,5,5-trimethyl-2-cyclohexen-1-one (11e) was prepared from *p*-hydroxybenzenethiol and epoxide **10** by a modification of the general procedure. After stirring at 0 °C for ~8 h, the reaction mixture was heated to reflux for ~2 h. Usual workup and crystallization from ether gave 2-(*p*-hydroxyphenylthio)-3,5,5-trimethyl-2-cyclohexen-1-one (70%, mp 183–184 °C): ^{1}H NMR gave singlets at δ 1.04 (6 H), 2.30 (3 H), 2.37 (2 H), 2.46 (2 H), and a multiplet at 6.4–7.2 (4 H); IR (Nujol) 2.95 (s), 6.00 (s), 6.23 (m), and 6.30 μ (s); electron impact mass spectrum *m/e* 262. Workup of the reaction mixture after 8 h at 0 °C gave a mixture of aldol isomers (87%), which underwent dehydration to **11e** under acid- (*p*-toluenesulfonic acid in refluxing benzene) or base-catalyzed conditions.

2-(2-Naphthylthio)-3,5,5-trimethyl-2-cyclohexen-1-one (11f) was prepared from 2-naphthalenethiol and epoxide **10** and crystallized from methylene chloride–methanol (96%, mp 111–112 °C); ^{1}H NMR gave singlets at δ 1.10 (6 H), 2.28 (3 H), 2.45 (2 H), 2.52 (2 H), and a multiplet at 7.1–7.9 (7 H).

2-(2-Methyl-1-naphthylthio)-3,5,5-trimethyl-2-cyclohexen-1-one (11g) was prepared from 2-methyl-1-naphthalenethiol (**50b**) and epoxide **10**, column chromatographed (no. 3 alumina, petroleum ether–benzene solvent), and crystallized from ether–petroleum ether (74%), mp 98.5–100 °C; ^{1}H NMR gave singlets at δ 0.92 (6 H), 2.05 (3 H), 2.16 (2 H), 2.25 (2 H), 2.71 (3 H), and multiplets at 7.0–7.8 (5 H) and 8.13–8.47 (1 H); electron impact mass spectrum *m/e* 310.

2-(2-Quinolylthio)-3,5,5-trimethyl-2-cyclohexen-1-one (11h) was prepared from 2-quinolinethiol[30] and epoxide **10**, column chromatographed (no. 3 alumina, methylene chloride–petroleum ether solvent), and crystallized from ether–petroleum ether (51%, mp 109–110 °C); ^{1}H NMR gave singlets at δ 1.20 (6 H), 2.22 (3 H), 2.37 (2 H), 2.46 (2 H), and a multiplet at 7.1–8.0; IR (chloroform) 5.95 (s), 6.04 (s), 6.18 (s), and 6.28 μ (s); electron impact mass spectrum *m/e* 297.

Anal. Calcd for $C_{18}H_{19}NOS$: C, 72.69; H, 6.44; N, 4.71; O, 5.38; S, 10.78. Found: C, 72.67; H, 6.51; N, 4.71; S, 10.77.

2-(3-Indolylthio)-3,5,5-trimethyl-2-cyclohexen-1-one (11i) was prepared from 3-indolethiol and epoxide **10**, column chromatographed (silica gel, benzene–petroleum ether solvent), and crystallized from ether–petroleum ether (mp ~74 °C); ^{1}H NMR gives singlets at δ 0.90 (6 H), 2.24 (2 H), 2.27 (2 H), 2.38 (3 H), and a multiplet at 7.0–7.9 (6 H); IR (Nujol) 2.91 (s), 6.00 (s), and 6.26 μ (m).

2-(1-Methyl-3-indolylthio)-3,5,5-trimethyl-2-cyclohexen-1-one (11j) was prepared from 1-methyl-3-indolethiol (**51b**) and epoxide **10** and crystallized from ether–petroleum ether (61%, mp 98–99 °C); ^{1}H NMR gave singlets at δ 0.92 (6 H), 2.23 (2 H), 2.28 (2 H), 2.40 (3 H), 3.69 (3 H), and multiplets at 6.9–7.4 (4 H) and 7.55–7.85 (1 H); IR (Nujol) 6.00 (s) and 6.33 μ (m).

2-(2-Benzothiazolylthio)-3,5,5-trimethyl-2-cyclohexen-1-one (11k) was prepared from 2-mercaptobenzothiazole[30] and epoxide **10** and crystallized from methylene chloride–methanol (88%, mp 117–119 °C); ^{1}H NMR gave singlets at δ 1.10 (6 H), 2.28 (3 H), 2.45 (2 H), 2.50 (2 H), and a multiplet at 7.1–7.9 (4 H).

2-(1-Naphthylthio)-2-cyclopenten-1-one (18) was prepared from 1-naphthalenethiol (**49d**) and 2-cyclopenten-1-one epoxide[31] and crystallized from ether–petroleum ether (90%, mp 76–76.5 °C); ^{1}H NMR gave multiplets centered at δ 2.51 (4 H), 6.47 (1 H, triplet, J = 2.5 Hz), and 7.3–8.4 (7 H); IR (neat) 5.85 (s), 6.32 (s), and 6.65 μ (s); electron impact mass spectrum *m/e* 240.

Anal. Calcd for $C_{15}H_{12}SO$: C, 74.99; H, 5.03. Found: C, 74.96; H, 5.17.

1-Phenylthio-$\Delta^{1(9)}$-octalone-2 (19) was prepared from benzenethiol

and the epoxide[9] of $\Delta^{1(9)}$-octalone-2[32] (82%, bp 187 °C at 0.15 mm); ^{1}H NMR gave a broad envelope at δ 1.0–2.8 (13 H) and a singlet at 7.17 (5 H); IR (neat) 5.95 (s), 6.30 (s), 13.52 (s), and 14.50 μ (s); electron impact mass spectrum *m/e* 258.

4-Phenylthiocholest-4-en-3-one (20a) was prepared from benzenethiol and 4β,5β-epoxycholestan-3-one[33] and crystallized from ether–petroleum ether (77%, mp 104–104.5 °C); ^{1}H NMR gave a broad envelope at δ 0.6–2.7 with superimposed sharp singlets at 0.73, 0.83, 0.92, 1.28, and 7.15; IR (Nujol) 5.94 (s), 6.30 (m), and 6.40 μ (s).

Anal. Calcd for $C_{33}H_{48}SO$: C, 80.44; H, 9.82. Found: C, 80.78; H, 9.34.

4-(2-Naphthylthio)cholest-4-en-3-one (20b) was prepared from 2-naphthalenethiol and 4β,5β-epoxycholestan-3-one[33] and crystallized from benzene (68%, mp 180–181 °C); ^{1}H NMR gave a broad envelope at δ 0.7–2.7 with superimposed singlets at 0.72, 0.83, 0.92, and 1.31 and a multiplet at 7.1–7.9; IR (Nujol) 5.94 μ (s).

Anal. Calcd for $C_{37}H_{50}SO$: C, 81.87; H, 9.29. Found: C, 81.50; H, 9.44.

3-Thiophenoxy-2,4-pentanedione (24). To a stirred solution of 3-chloro-2,4-pentanedione (22.66 g, 0.169 mol) in pyridine (16 mL) at 0 °C was slowly added a solution of benzenethiol (23 mL, 0.224 mol) in methanol (20 mL). After stirring for 6 h at room temperature, solvent was evaporated and the residue extracted with carbon tetrachloride (100 mL). The resulting solution was washed with 0.3 N hydrochloric acid (3 × 25 mL) and water (3 × 25 mL), dried over anhydrous magnesium sulfate, and evaporated; distillation gave **24** (87%, bp 93–95 °C at 0.04 mm).

3-Thiophenoxy-4-methyl-3-penten-2-one (26). To a stirred suspension of sodium hydride (2.55 g, 0.106 mol) in ether (20 mL) at ice bath temperature was slowly added a solution of **24** (21.20 g, 0.101 mol) in ether (100 mL). After stirring for 1 h at room temperature and then cooling to 0 °C, a solution of methylmagnesium bromide (50 mL of a 2.8 M, 0.140 mol) in ether was slowly added and the resulting mixture was stirred at room temperature for 2 days. Acetic anhydride (25 mL) was then added and the solution was refluxed for 2.5 h. After cooling to 0 °C, water (200 mL) was added. The organic layer was separated, washed with 1 N sodium hydroxide (3 × 50 mL), 1 N sodium bisulfide (1 × 50 mL), and water (3 × 50 mL), dried over anhydrous magnesium sulfate, and evaporated. Distillation gave **26** (75%, bp 83–85 °C at 0.03 mm); ^{1}H NMR gave singlets at δ 2.10 (3 H), 2.13 (3 H), 2.26 (3 H), and 7.24 (5 H); IR (neat) 5.95 (s) and 6.30 μ (s).

Anal. Calcd for $C_{12}H_{14}OS$: C, 69.86; H, 6.84. Found: C, 69.81; H, 6.84.

Irradiation of 2-Phenylthio-3,5,5-trimethyl-2-cyclohexen-1-one (11a). General Photochemical Procedure for Dihydrothiophene Formation. A solution of **11a** (70.4 g) in benzene (1500 mL) and methanol (500 mL) was placed in the preparative photoreactor and dry argon was passed into the solution for 30 min prior to and during irradiation. After 20 h, <0.5% **11a** was present in the nearly colorless reaction mixture (VPC analysis on 6 ft × $\frac{1}{8}$ in. stainless steel column filled with 10% UC-W98 on Chromosorb W, 80–100 mesh size at 200 °C). Evaporation and crystallization from ether–petroleum ether gave **12a** (91%, mp 80–82 °C); ^{1}H NMR gave sharp singlets at δ 0.75 (3 H), 1.09 (3 H), 1.46 (3 H), a broadened singlet at 3.83 (1 H), and multiplets at 1.6–2.8 (4 H) and 7.0–7.3 (4 H); IR (Nujol) 5.84 (s) and 13.2 μ (s).

Irradiation of 2-(o-tolylthio)-3,5,5-trimethyl-2-cyclohexen-1-one (11b) was performed on a 4.9-g scale. Crystallization from ether–petroleum ether gave **12b** (88%, mp 100–102 °C); ^{1}H NMR gave sharp singlets at δ 0.75 (3 H), 1.05 (3 H), 1.42 (3 H), 2.25 (3 H), a broadened singlet at 3.80 (1 H), and multiplets at 1.6–2.8 (4 H) and 6.8–7.2 (3 H).

Irradiation of 2-(*m*-tolylthio)-3,5,5-trimethyl-2-cyclohexen-1-one (11c) was performed on a 4.7-g scale; distillation gave a (70:30) mixture of two dihydrothiophenes **12c** (92%, bp 147–150 °C at 0.02 mm). The mixture was separated by preparative VPC on a 6 ft × $\frac{1}{4}$ in. aluminum column filled with 10% Dow-11 on Chromosorb W, 80–100 mesh size at 180 °C. The first material collected was the minor isomer; ^{1}H NMR gave sharp singlets at δ 0.77 (3 H), 1.07 (3 H), 1.42 (3 H), 2.29 (3 H), and a broadened singlet at 3.79 (1 H). The second material collected gave sharp singlets at δ 0.95 (3 H), 1.07 (3 H), 1.58 (3 H), 2.43 (3 H), and a broadened singlet at 3.79 (1 H).

Irradiation of 2-(*p*-tolylthio)-3,5,5-trimethyl-2-cyclohexen-1-one (11d) was performed on a 3.8-g scale. Distillation gave **12d** (84%, bp 140–143 °C at 0.1 mm); ^{1}H NMR gave shapr singlets at δ 0.78 (3 H), 1.08 (3 H), 1.45 (3 H), 2.31 (3 H), a broadened singlet at 3.81 (1 H), and multiplets at 1.6–2.8 (4 H) and 6.8–7.2 (3 H); IR (neat) 5.80 (s), 11.4 (m), and 12.35 μ (s); electron impact mass spectrum *m/e* 260.

Irradiation of 2-(*p*-hydroxyphenylthio)-3,5,5-trimethyl-2-cyclohexen-1-one (11e) was performed on a 3.3-g scale. Crystallization from ether gave **12e** (83%, mp 125–128 °C); ^{1}H NMR gave sharp singlets at δ 0.76 (3 H), 1.06 (3 H), 1.42 (3 H), boradened singlets at 3.82 (1 H) and 5.80 (1 H, disappears on addition of deuterium oxide), and multiplets at 1.6–2.8 and 6.5–7.2; IR (chloroform) 2.95 (s), 5.88 (s), 6.24 (m), and 6.32 μ (s); IR (Nujol) 5.80 (s) and 5.90 μ (s).

Irradiation of 2-(2-naphthylthio)-3,5,5-trimethyl-2-cyclohexen-1-one (11f) was performed on a 14-g scale. Distillation gave **12f** (89%, bp 210–212 °C at 0.3 mm); ^{1}H NMR gave sharp singlets at δ 0.68 (3 H), 1.04 (3 H), 1.71 (3 H), a doublet centered at 3.85 (1 H, 1.5 Hz), and multiplets at 1.7–2.9 (4 H) and 7.1–8.2 (6 H).

Oxidation of **11f** with *m*-chloroperbenzoic acid by the procedure described for preparation of **6b** gave a crystalline sulfone derivative (83%, mp 182–183 °C): IR (Nujol) 5.83 (s), 7.68 (s), and 8.91 μ (s); electron impact mass spectrum *m/e* 328.

Irradiation of 2-(2-methyl-1-naphthylthio)-3,5,5-trimethyl-2-cyclohexen-1-one (11g) was performed on a 100-mg scale in 3.2 mL of solvent, 96-h irradiation. Evaporation of solvent and ^{1}H NMR analysis revealed a clean mixture of two components identified as 2-methyl-1-naphthol (**30**) [^{1}H NMR δ 2.38 (3 H, singlet), 5.25 (1 H, broad singlet, disappears on addition of deuterium oxide), 7.2–8.3 (6 H, complex multiplet)] and enethiol **31;** [^{1}H NMR δ 1.00 (6 H, singlet), 2.01 (3 H, singlet), 2.2–2.5 (4 H, multiplet), and 4.52 (1 H, singlet)]. Extraction of a methylene chloride solution (20 mL) of the crude reaction mixture with 1 N sodium hydroxide (2 × 10 mL), acidification of the aqueous layer with 1 N hydrochloric acid and extraction with methylene chloride (3 × 10 mL), drying over anhydrous magnesium sulfate, and evaporation gave a nearly pure mixture of **30** and **31** (^{1}H NMR and VPC analysis on a 6 ft × $\frac{1}{8}$ in. glass column filled with 5% SE-30 on Gas Chrom Q, 100/120 mesh size; temperature programmed 4 min at 100 °C to 200 °C at 16 °C/min; retention time **31** 8.0 min, **30** 9.2 min); VPC–mass spectral analysis **30,** electron impact mass spectrum, *m/e* 158; **31,** chemical ionization mass spectrum, *m/e* 171.

Irradiation of 2-(2-quinolylthio)-3,5,5-trimethyl-2-cyclohexen-1-one (11h) was performed on a 3.6-g scale. Column chromatography (alumina, 10% methylene chloride–petroleum ether solvent) and crystallization from methylene chloride–petroleum ether gave **12h** (77.5%, mp 165–166 °C); ^{1}H NMR gave sharp singlets at δ 0.80 (3 H), 1.13 (3 H), 1.60 (3 H), a broadened singlet at 3.98 (1 H), and multiplets at 1.7–2.8 (4 H) and 7.2–8.1 (5 H); IR (chloroform) 5.80 μ (s); electron impact mass spectrum *m/e* 297.

Anal. Calcd for $C_{18}H_{19}NOS$: C, 72.69; H, 6.44; N, 4.71; O, 5.38; S, 10.78. Found: C, 72.67; H, 6.41; N, 4.69; S, 10.70.

Irradiation of 2-(3-indolylthio)-3,5,5-trimethyl-2-cyclohexen-1-one (11i) was performed on a 116-mg scale in 3.2 mL of solvent and followed by ^{1}H NMR spectroscopy. Irradiation produced polymeric-appearing reaction products.

Irradiation of 2-(1-methyl-3-indolylthio)-3,5,5-trimethyl-2-cyclohexen-1-one (11j) was performed on a 4.9-g scale. Crystallization from ether gave **12j** (63%, mp 144–146 °C); ^{1}H NMR gave sharp singlets at δ 0.87 (3 H), 1.05 (3 H), 1.50 (3 H), 3.70 (3 H), a doublet at 4.04 (1 H, J = 1.8 Hz), and multiplets at 1.5–2.9 (4 H) and 6.9–7.5 (4 H).

Irradiation of 2-(2-Benzothiazolylthio)-3,5,5-trimethyl-2-cyclohexen-1-one (11k) was performed on a 100-mg scale in 3.2 mL of solvent and monitored by ^{1}H NMR spectroscopy. Essentially no reaction was observed up to 24 h of irradiation; extended irradiation eventually resulted in photopolymerization.

Irradiation of 2-(naphthylthio)-2-cyclopenten-1-one (18) was performed on a 0.58-g scale. Crystallization from ether gave **33** (86%, mp 96–96.5 °C); ^{1}H NMR gave multiplets at δ 2.2–2.5 (4 H), 4.1–4.4 (2 H), and 7.1–8.0 (6 H); IR (neat, oil) 5.90 (s), 12.45 (s), and 13.25 μ (s); electron impact mass spectrum *m/e* 240.

Anal. Calcd for $C_{15}H_{12}SO$: C, 74.99; H, 5.03. Found: C, 74.99; H, 4.91.

Extended irradiation of **18** or irradiation in the presence of atmospheric oxygen produced **34,** which crystallized from the irradiation solution (mp 221 °C). ^{1}H NMR gave resonances centered at δ 3.12 (4 H) and 7.2–8.2 (6 H); IR (Nujol) 5.90 μ (s); electron impact mass spectrum *m/e* 238.

Anal. Calcd for $C_{15}H_{10}SO$: C, 75.62; H, 4.23. Found: C, 75.61; H, 4.32. Thiophene **34** also was formed on treatment of **33** with DDQ (see experimental procedure for DDQ dehydrogenation of **6a**).

Irradiation of 1-phenylthio-$\Delta^{1(9)}$-octalone-2 (19) was performed on a 170-mg scale. Evaporation of solvent gave **35** as a nearly colorless oil (>95% purity by NMR and VPC analysis on a 3 ft × 1/8 in. glass column filled with 5% Dexsil on Gas Chrom Q, 100/120 mesh size at 230 °C; retention time for **35** was 3.6 min and **19** was 4.8 min): IR (neat) 5.85 (s) and 13.3 μ (s).

Irradiation of 4-phenylthiocholest-4-en-3-one (20a) was performed on a 2.17-g scale with a Corning uranyl glass filter employed.[3] Crystallization from benzene gave **38a** (90%, mp 173.4–174.3 °C); ^1H NMR gave singlets at δ 0.70, 0.83, 0.93, 1.12, and 4.25; electron impact mass spectrum *m/e* 492.

Anal. Calcd for $C_{33}H_{48}SO$: C, 80.44; H, 9.82. Found: C, 80.46; H, 9.79.

Irradiation of 4-(2-naphthylthio)cholest-4-en-3-one (20b) was performed on a 0.45-g scale with a Corning uranyl glass filter employed. Crystallization from benzene gave **38b** (69%, mp 229–230 °C); ^1H NMR gave singlets at δ 0.75, 0.83, 0.94, 1.14, and 4.31; electron impact mass spectrum *m/e* 542.

Anal. Calcd for $C_{37}H_{50}SO$: C, 81.87; H, 9.29. Found: C, 81.50; H, 9.44.

Irradiation of 3-thiophenoxy-4-methyl-3-penten-2-one (26) was performed on a 144-mg scale in benzene–methanol–acetic acid (1:1:1). After irradiation was complete, ether (25 mL) was added and the resulting solution was washed with water (2 × 10 mL), 1 N sodium bicarbonate (3 × 10 mL), water (2 × 10 mL), and saturated sodium chloride (1 × 10 mL), dried over anhydrous magnesium sulfate, and distilled in a Kugelrohr apparatus to give pure **39** (84%, bp 121–123 °C at 0.02 mm); ^1H NMR gave sharp singlets at δ 1.36 (3 H), 1.42 (3 H), 2.10 (3 H), 3.94 (1 H), and a multiplet at 7.05–7.31 (4 H); IR (neat) 5.90 μ (s).

Anal. Calcd for $C_{12}H_{14}SO$: C, 69.86; H, 6.84. Found: C, 69.81; H, 6.84.

Desulfurization of Dihydrothiophene 12a. General Procedure. To a stirred suspension of freshly prepared Raney Nickel (prepared from 60 g of Raney nickel–aluminum alloy)[34] in ethanol (70 mL) was added **12a** (7.00 g). The mixture was heated to reflux and VPC analysis indicated that all **12a** was consumed in ~30 min. While warm, the reaction mixture was filtered under vacuum through a pad of Celite and the filter cake was thoroughly washed with warm ethanol (~200 mL). Care was taken to ensure that the nickel residue remained wet with solvent to prevent ignition. Evaporation of solvent gave a colorless oil (6.2 g), which had undergone some carbonyl reduction (NMR and IR analysis). To a solution of the oil in acetone (30 mL) at 0 °C was added Jones reagent and after stirring for 1 h at room temperature, 2-propanol was added dropwise. Water (100 mL) and ether (200 mL) were added, and the organic layer was separated and washed with 1 N sodium bicarbonate and saturated sodium chloride (1 × 25 mL), dried over anhydrous magnesium sulfate, and distilled to give 3-phenyl-3,5,5-trimethylcyclohexanone (**13a,** 85%, bp 110–111 °C at 0.1 mm); ^1H NMR gave sharp singlets at δ 0.40 (3 H), 1.05 (3 H), 1.38 (3 H), and multiplets at 1.7–3.3 (6 H) and 7.1–7.5 (5 H); IR (neat) 5.85 (s), 13.12 (s), and 14.29 μ (s).

Desulfurization of 12b. Distillation gave 3-(*m*-tolyl)-3,5,5-trimethylcyclohexanone (**13b,** 87%, bp 130–131 °C at 0.2 mm); ^1H NMR gave sharp singlets at δ 0.43 (3 H), 1.03 (3 H), 1.34 (3 H), 2.33 (3 H), and multiplets at 1.7–3.3 (6 H) and 6.8–7.3 (4 H); electron impact mass spectrum *m/e* 230.

Desulfurization of 12d. Distillation gave 3-(*m*-tolyl)-3,5,5-trimethylcyclohexanone (**13b,** 86%), identical with the product of desulfurization of **12b** (^1H NMR, IR, and VPC analysis).

Desulfurization of 12e. Distillation gave 3-(*p*-hydroxyphenyl)-3,5,5-trimethylcyclohexanone (**13e,** 83%, bp 165–167 °C at 0.1 mm); ^1H NMR gave sharp singlets at δ 0.45 (3 H), 1.03 (3 H), 1.34 (3 H), multiplets at 1.7–3.3 (6 H) and 6.5–7.4 (4 H), and a broad resonance at ~8.1 (1 H); IR (neat) 3.00 (s), 5.88 (s), 6.30 (s), 11.60 (m), 12.80 (s), and 14.20 μ (s).

Desulfurization of 12f. ^1H NMR spectroscopy of the product from the Jones reaction showed substantial hydrogenation of the naphthalene ring. Treatment with DDQ (see experimental procedure for DDQ dehydrogenation of **6a**) and distillation gave **13f** (50%, bp 154–157 °C at 0.2 mm); ^1H NMR gave singlets at δ 0.16 (3 H), 1.00 (3 H), 1.74 (3 H), and multiplets at 1.8–3.5 (6 H) and 7.1–8.0 (7 H).

Desulfurization of 35. Preparative TLC (silica gel, benzene solvent) gave *cis*-9-phenyldecalone-2 (**40,** oil, 55% from thiophenoxyenone **19**). This material was identical with that prepared from addition of lithium diphenylcuprate to $\Delta^{1(9)}$-octalone-2[19] (^1H NMR, especially the C(1) methylene which gave an AB quartet centered at δ 2.55 and 2.87, J_{AB} = 15 Hz; IR, VPC, and mass spectral fragmentation analysis).

Reductive Cleavage of 13a. A stirred solution of dihydrothiophene **13a** (10.0 g) in glacial acetic acid (75 mL), together with zinc dust (60 g), was heated at reflux for 24 h. The water condenser was replaced by a 14-in. distillation column and the acetic acid was removed at aspirator pressure. Benzene (50 mL) and ether (50 mL) were added to the residue and the resulting mixture was stirred and filtered through a pad of Celite. This washing procedure was twice repeated and the combined organic layers were evaporated and crystallized from ether–petroleum ether to give **14** (94%, mp 127–129 °C); ^1H NMR gave sharp singlets at δ 0.70 (3 H), 0.92 (3 H), 1.38 (3 H), and a broad singlet at 4.6 (1 H, disappears on addition of deuterium oxide); IR (Nujol) 2.95 (s) and no absorption in the region 5–6 μ; electron impact mass spectrum *m/e* 248 (100%), M-17 (10%).

Anal. Calcd for $C_{15}H_{20}OS$: C, 72.53; H, 8.12; S, 12.91. Found: C, 72.50; H, 8.10; S, 12.88.

Conversion of 14 to Dihydrothiophene 13a. A solution of **14** (500 mg, 2.02 mmol) and *p*-toluenesulfonyl chloride (390 mg, 2.05 mmol) in pyridine (2 mL) was heated to reflux in a nitrogen atmosphere for 6 h. Ether (50 mL) was added and the resulting solution was washed with 1 N sodium carbonate (3 × 30 mL), dried over anhydrous magnesium sulfate, and evaporated to give crystalline **13a** (100%).

4-Phenylthio-1-buten-3-one (44). A solution of 1,4-diazabicyclo[2.2.2]octane (Dabco, 11.6 g, 0.104 mol) and thioanisole (**42,** 12.4 g, 0.100 mol) in THF (125 mL) was stirred in a nitrogen atmosphere at ice-bath temperature, while a solution of *n*-butyllithium in hexane (70 mL, 2.0 M, 0.140 mol) was added over 30 min. The resulting dark red solution was stirred at room temperature for 1 h and was then cooled to −78 °C. A solution of acrolein (18.0 g, 0.322 mol) in THF (50 mL) was added over 30 min, after which the cooling bath was removed and stirring continued for 5 h. Addition of ammonium chloride solution was followed by extraction with ether (2 × 200 mL), drying over anhydrous magnesium sulfate, and distillation to give a vinyl alcohol (67.5%, 108–113 °C at 0.20 mm) identical by ^1H NMR and IR spectroscopy with previously reported[35] 4-phenylthio-1-buten-3-ol (**43**).

A solution of 4-phenylthio-1-buten-3-ol (23.0 g, 0.128 mol) and freshly prepared chromium trioxide–pyridine complex (Sarett reagent, 17.0 g, 0.129 mol) was stirred at 0 °C for 5 min. The mixture was quickly filtered under vacuum through a pad of Celite and evaporated to ~50 mL and ether (500 mL) was added. Vacuum filtration through a pad of anhydrous magnesium sulfate, evaporation, and distillation gave **44** (69%, bp 93–97 °C at 0.1 mm); ^1H NMR gave a singlet at δ 3.80 (2 H) and a multiplet at 7.1–7.5 (5 H); the olefinic protons gave clearly defined pairs of doublets centered at δ 6.50 and 6.79 for H_a (J_{ab} = 9.5, J_{ac} = 17.5 Hz), 5.73 and 5.88 for H_b (J_{ba} = 9.5, J_{bc} = 2.7 Hz), and 6.07 and 6.36 for H_c (J_{ca} = 17.5, J_{cb} = 2.7 Hz); IR (neat) 5.88 (s), 6.14 (s), and 6.25 μ (m).

1-Phenylthio-$\Delta^{1(9)}$-octalone-2 (19). Annelation of Pyrrolidine Enamine of Cyclohexanone with 44. A solution of the pyrrolidine enamine of cyclohexanone[21] (0.90 g, 6.0 mmol) and **44** (0.74 g, 4.2 mmol) in *p*-dioxane (20 mL) was heated to reflux for 9 h in a nitrogen atmosphere. A sodium acetate–acetic acid buffer[21] was added and refluxing was continued for 5 h. About 30 mL of solvent was removed by distillation, water (50 mL) was added to the residue, and the resulting mixture was extracted with ether (4 × 25 mL). The organic layer was washed with 1 N hydrochloric acid (1 × 10 mL), 1 N sodium hydroxide (1 × 10 mL), and saturated sodium chloride solution (1 × 10 mL), dried over anhydrous magnesium sulfate, and distilled to give **19** (51%, bp 164–166 °C at 0.15 mm). This material was identical with that prepared from the epoxide of $\Delta^{1(9)}$-octalone-2 (^1H NMR, IR, and VPC analysis).

Oxidation of 12a. A solution of **12a** (1.00 g) in acetone (10 mL) was stirred at room temperature and Jones reagent (5 equiv) was added dropwise. After 2 h, filtration of the crystalline precipitate, followed by a water wash and recrystallization from chloroform–ether, gave **46b** (88%, mp 186–187 °C); ^1H NMR gave singlets at δ 1.08 (3 H), 1.12 (3 H), 1.60 (3 H), and 5.2 (1 H, disappears on addition of deuterium oxide), and multiplets at 1.7–3.4 (4 H) and 7.3–7.9 (4 H); IR (chloroform) 2.80 (m), 5.81 (s), 7.65 (s), 8.67 (s), and 8.94 μ (s);

chemical ionization mass spectrum *m/e* 295.

Reaction of 46b with Aqueous Sodium Hydroxide. Hydroxy sulfone **46b** (1.00 g) in 1 N sodium hydroxide was heated to reflux for 24 h. Addition of 1 N hydrochloric acid to pH <2, continuous extraction with chloroform, and crystallization from ether gave sulfinate ester **47** (75%, mp 205–207 °C); ^{1}H NMR gave singlets at δ 1.12 (3 H), 1.34 (3 H), 1.38 (3 H), 2.23 (2 H), 9.04 (1 H, disappears on addition of deuterium oxide), an AB quartet centered at 1.89 (1 H) and 2.65 (1 H, J_{AB} = 13 Hz), and a multiplet at 7.0–7.7 (4 H); IR (Nujol) 3.0–4.3 (s), 5.73 (s), 5.84 (s), and 8.99 μ (s);[23] IR (chloroform) one carbonyl absorption 5.78 μ (s); chemical ionization mass spectrum *m/e* 295.

Anal. Calcd for $C_{15}H_{18}O_4S$: C, 61.20; H, 6.16. Found: C, 61.13; H, 6.18.

Methylation of 12a. To a suspension of potassium hydride (128 mg, 3.20 mmol) in THF (5 mL) in a nitrogen atmosphere was added dihydrothiophene **12a** (0.81 g, 3.29 mmol). After 2 h of equilibration, excess methyl iodide was added and the mixture was stirred at room temperature for 8 h. Water (10 mL) was added and the resulting mixture was extracted with chloroform (3 × 25 mL). The organic layer was washed with water (1 × 10 mL), dried over anhydrous magnesium sulfate, evaporated, and crystallized from chloroform–petroleum ether to give **12b** (72%, mp 72–74 °C); ^{1}H NMR gave singlets at δ 0.88 (3 H), 1.02 (3 H), 1.35 (3 H), 1.50 (3 H), and multiplets at 1.4–2.9 (4 H) and 7.0–7.3 (4 H).

Oxidation of 12b. Employing the procedure for oxidation of **12a**, except that reaction time was 48 h, **12b** (0.5-g scale) gave after crystallization from chloroform–ether **46c** (75%, mp 109–113 °C); ^{1}H NMR gave singlets at δ 1.01 (3 H), 1.04 (3 H), 1.49 (3 H), 1.53 (3 H), and multiplets at 1.5–2.8 (4 H) and 7.3–7.9 (4 H); IR (Nujol) 5.85 (s), 7.70 (s), and 8.67 μ (s).

Reaction of 46c with Aqueous Sodium Hydroxide. Employing the procedure for rearrangement of **46b, 46c** gave, after crystallization from ether–chloroform, carboxylic acid **48** (70%, mp 148–152 °C); ^{1}H NMR gave singlets at δ 0.88 (3 H), 1.08 (3 H), 1.28 (3 H), 2.28 (2 H), a doublet centered at 1.51 (3 H, J = 7 Hz), an AB quartet centered at 1.92 (1 H) and 2.48 (1 H, J_{AB} = 16 Hz), a quartet centered at 3.82 (1 H, J = 7 Hz), a multiplet at 7.2–7.9 (4 H), and a broad resonance at 10.0 (1 H, disappears on addition of deuterium oxide); IR (Nujol) 2.6–4.0 (s), 5.80 (s), 7.70 (s), 8.55 (s), and 8.60 μ (s).

1-Naphthalenethiol (49d) was prepared from naphthalene by literature procedures,[25] bp 115 °C at 0.9 mm.

2-Methyl-1-naphthalenethiol (50b).[26] A solution of 1-bromo-2-methylnaphthalene (**50a,** 18.7 g, 84.4 mmol) in THF (100 mL) was added dropwise to a stirred suspension of magnesium turnings (2.2 g, 91.8 mmol) in THF (20 mL) in a nitrogen atmosphere at a rate necessary to maintain reflux (a small crystal of iodine was added). When addition was complete, the mixture was heated to reflux for 45 min and then cooled in an ice bath for 15 min. Sulfur (2.75 g, 86.0 mmol) was added to the cooled mixture over 30 min, after which the mixture was stirred at room temperature for 2 h. Saturated ammonium chloride (50 mL) was added and the solution was vacuum filtered through a Celite pad. The precipitate was washed with saturated ammonium chloride (50 mL) and ether (2 × 100 mL). After separation of layers, the organic solution was washed with saturated sodium chloride, dried over anhydrous magnesium sulfate, and distilled to give **50b** (61%, bp 150–156 °C at 0.7 mm); ^{1}H NMR gave singlets at δ 2.60 (3 H), 3.38 (1 H), and multiplets at 7.2–7.9 (5 H) and 8.23 (1 H); IR (neat) 3.92 μ (w).

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References and Notes

(1) (a) Postdoctoral research associate, 1973–1975. (b) Predoctoral student, 1972–1977.
(2) Undergraduate research participant, 1974–1975.
(3) A. G. Schultz and M. B. DeTar, *J. Am. Chem. Soc.*, **98**, 3564 (1976).
(4) M. Karplus, *J. Am. Chem. Soc.*, **85**, 2870 (1963), and ref 1.
(5) W. E. Truce and F. M. Perry, *J. Org. Chem.*, **30**, 1316 (1965).
(6) Other methods for introduction of an aryl nucleus at an enolate carbon atom include enolate trapping with arynes [J. F. Bunnett, *Q. Rev., Chem. Soc.*, **12**, 1 (1958); R. Gompper, G. Seybold, and B. Schmolke, *Angew. Chem., Int. Ed. Engl.*, **7**, 389 (1968)] and with diaryliodonium salts [F. M. Beringer, W. J. Daniel, S. A. Galton, and G. Rubin, *J. Org. Chem.*, **31**, 4315 (1966)] and photoinitiated substitution of aryl halides [J. F. Bunnett and J. E. Sundberg, *ibid.*, **41**, 1702 (1976); M. F. Semmelhack and T. M. Bargar, *ibid.*, **42**, 1481 (1977), and references cited therein]. For the α-arylation of α,β-unsaturated ketones via epoxytosylhydrazones, see P. L. Fuchs, *ibid.*, **41**, 2935 (1976); G. Stork and A. A. Pnaras, *ibid.*, **41**, 2937 (1976).
(7) G. H. Posner, *Org. React.*, **19**, 1 (1972).
(8) A preliminary account of a portion of this work has been reported in communication form; see A. G. Schultz, *J. Org. Chem.*, **39**, 3185 (1974).
(9) E. I. Wasson and H. O. House, *Org. Synth.*, **37**, 58 (1957).
(10) See P. M. McCurry and R. K. Singh, *J. Org. Chem.*, **39**, 2316 (1974), and S. Danishefsky and A. Zimmer, *ibid.*, **41**, 4059 (1976), for recent studies of the factors controlling the direction of base-catalyzed aldol cyclizations of 1,4- and 1,5-diketones, respectively.
(11) A. G. Schultz, R. D. Lucci, W. Y. Fu, M. H. Berger, J. Erhardt, and W. K. Hagmann, *J. Am. Chem. Soc.*, following paper in this issue.
(12) Similar experimental results were reported by M. A. Tobias, J. G. Strong, and R. P. Napier, *J. Org. Chem.*, **35**, 1709 (1970).
(13) G. Büchi and H. Wüest, *Helv. Chim. Acta*, **54**, 1767 (1971).
(14) The cis isomer is the more stable in the perhydroindanone series; see H. O. House and R. G. Carlson, *J. Org. Chem.*, **29**, 74 (1964).
(15) For example, stabilized mesoionic oxazolones have been isolated; see R. Huisgen, H. Gotthardt, H. O. Bayer, and F. C. Schaefer, *Angew. Chem., Int. Ed. Engl.*, **3**, 136 (1964); M. Hamaguchi and T. Ibata, *Tetrahedron Lett.*, 4475 (1974). Electronic stabilization of azomethine ylides generated from photochromic aziridines also has been noted; see T. DoMinh and A. M. Trozzolo, *J. Am. Chem. Soc.*, **94**, 4406 (1972), and references cited therein.
(16) We thank L. Cate for preparation and irradiation of **18.** The preparation of **26** and preliminary photochemical studies have been performed by W. K. Hagmann.
(17) A. G. Schultz and W. Y. Fu, *J. Org. Chem.*, **41**, 1483 (1976); A. G. Schultz and R. D. Lucci, *J. Chem. Soc., Chem. Commun.*, 925 (1976).
(18) Recent key studies in this area include the elegant experiments described by J. C. Dalton and F. C. Montgomery, *J. Am. Chem. Soc.*, **96**, 6230 (1974).
(19) S. M. McElvain and D. C. Remy, *J. Am. Chem. Soc.*, **82**, 3690 (1960).
(20) E. J. Corey and D. Seebach, *J. Org. Chem.*, **31**, 4097 (1966).
(21) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963).
(22) For excellent reviews of annelation reactions, see M. E. Jung, *Tetrahedron*, **32**, 3 (1976); W. R. Kenan, *Synthesis*, 777 (1976).
(23) D. Darwish and E. A. Preston, *Tetrahedron Lett.*, 113 (1964).
(24) C. A. Brown, *J. Org. Chem.*, **39**, 1324 (1974).
(25) L. Gattermann, "Laboratory Methods of Organic Chemistry", Macmillan, New York, N.Y., 1943, Chapter 4.
(26) C. H. J. G. Muller and P. Cagniant, *C. R. Acad. Sci., Ser. C*, **264**, 455 (1967).
(27) H. Gilman and L. Fullhart, *J. Am. Chem. Soc.*, **71**, 1478 (1949).
(28) Thiol **51b** was prepared by modification of a procedure described by R. L. N. Harris, *Org. Synth.*, submitted (1972).
(29) The exclusion of atmospheric oxygen is very important for high-yield preparation of **12.** Using our procedure for synthesis of **12a,** but in the presence of oxygen, Zoretic isolated a substance which gives a ^{1}H NMR spectrum and mass spectral fragmentation pattern consistent with rearranged enone **17** (Ar = Ph). We thank Professor Zoretic for this interesting observation and a sample of the material for the spectral identification.
(30) Aldrich Chemical Co., Inc.
(31) H. O. House and R. L. Wasson, *J. Am. Chem. Soc.*, **79**, 1488 (1957); C. S. Markos and W. Reusch, *ibid.*, **89**, 3363 (1967).
(32) R. L. Augustine and J. A. Caputo, *Org. Synth.*, **45**, 80 (1965).
(33) H. B. Henbest and W. R. Jackson, *J. Chem. Soc. C*, 2459 (1967).
(34) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. 1, Wiley, New York, N.Y., 1967, p 729.
(35) A. A. Oswald, K. Griesbaum, and B. E. Hudson, *J. Org. Chem.*, **28**, 2355 (1963).